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COMPLETE SPECIFICATION

Method and Apparatus for Automatic Analyzing

I, CLIFFORD CHARLES HACH, a citizen of the United States of America, of Box 194, R.R. 3, Meadow Glen Road, Ames, Iowa, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The invention relates to apparatus for and a method of automatic analysis.

15 According to the invention there is provided an automatic analyzer which comprises means for feeding a stream of a sample at a constant head through a first capillary metering passage, means for feeding a stream of a reagent at a predetermined head through a second capillary metering passage into the sample stream at a position upstream or 20 downstream of the first passage and separated from the first passage by a passage of non-metering dimensions, means for mixing the sample-reagent stream and means for detecting a reaction in the mixed sample reagent stream.

25 In a particular analyzer according to the invention the means for detecting a reaction comprise a colourimeter having means for maintaining a constant and uniform flow of the sample reagent mixture through the 30 colourimeter cell. Preferably the colourimeter comprises a transparent generally vertically disposed cell having an open top and open bottom, a transparent chamber surrounding the cell, the lower end of the cell opening 35 into the chamber, an overflow outlet formed in the chamber above the lower end of the cell, and means for dripping the sample reagent stream into the cell so as to mix the sample and reagent.

40 The analyzers are adapted to perform continuous titration. In this application an ana-

lyzer according to the invention is provided comprising means, upstream of the means for mixing the sample reagent stream, for feeding in a stream of an indicator, means for detecting a reaction in the mixed stream indicative of an end point, and means, responsive to the detecting means, for varying the head of the reagent so that the head is continuously alternately raised and lowered to bring the mixed stream repeatedly to the end point.

55 According to the invention furthermore there is provided a method of continuously performing a test on a sample comprising the steps of creating a steady and uniform stream of the sample, adding to the stream a constant and uniform flow of reagent, dripping the sample reagent stream into a cell so as to mix the stream flowing the sample reagent mixture constantly and uniformly through the cell, and detecting any reaction caused. In the method as applied to continuous titration there are comprised the steps of creating a steady and uniform stream of the sample, adding to the stream a constant and uniform flow of a reagent, adding to the sample reagent stream a flow of an indicator, mixing the sample reagent indicator stream in a cell, flowing the mixed stream constantly and uniformly through the cell, detecting an end point reaction in the cell, and alternately reducing and increasing the amount of reagent added to the stream so as to repeatedly bring the mixture in the cell to end point.

80 The invention is illustrated, by way of example, in the accompanying diagrammatic drawings, in which:—

Figure 1 is an automatic analyzer;

Figure 2 is an automatic analyzer particularly intended for spectrophotometric titration; and

[Price 4s. 6d.]

Figure 3 is a wiring diagram of the of the analyzer shown in Figure 2.

The analyzer of Figure 1 is particularly intended for continuous colorimetric testing of a fluid sample 11 by using measured quantities of a known fluid reagent 12.

In the analyzer, the reaction is detected by a colourimeter 15 whose electrical output is indicated by a galvanometer 16. The galvanometer 16 gives a continuous reading reflecting the extent of colour change produced by the reaction of the sample 11 and reagent 12 in the colourimeter 15. Hence, by knowing the nature and concentration of the reagent 12, and the amounts of sample and reagent being continuously brought together, the analyzer 10 accurately indicates the presence and concentration of the unknown in the sample under test.

In order to create a steady and uniform stream of the sample 11, the sample is fed at a constant head pressure through a capillary metering tube 21. A conduit 22 conducts the sample through a flow-control cock 23 to a mixing passage 24. The metering tube 21, conduit 22 and passage 24 are all fixed relative to one another by a common frame 25. The metering tube 21 and the passage 24 are defined by suitably formed glass tubing which is embedded in a plastic frame block 26 to protect the glass parts and hold them in the desired relative positions.

To maintain a constant head pressure on the sample 11 in the passage 24, an up-standing overflow outlet or passage 27 is mounted on the frame 25 in communication with the passage 24. The fluid overflowing from the outlet 27 spills into a conduit 29 that is connected to a drain 30. An open-top sight glass 28 is also provided to indicate visually the head of the sample. The cock 23 is adjusted to provide a sample flow of 100 mls./min. The capillary metering tube 21 is formed of such a length and diameter as to pass 5 mls./min. with the particular sample head established by the overflow outlet 27. The fluid sample which does not pass through the metering tube 21 is simply spilled through the overflow outlet 27 to the drain 30 as is shown by the flow arrows appearing in Figure 1 in the passage 24.

For adding a steady and uniform stream of reagent 12 to the stream of the sample, the reagent is fed to the passage 24 at a predetermined head pressure through a capillary metering tube 31. The reagent 12 is contained in a five quart plastic bag 32 supported within a carton 33 and is fed to the metering tube through a conduit 34. A sight glass 35 provides an indication of the amount of reagent solution remaining in the bag 32.

To maintain a predetermined head pressure on the reagent 12, a float valve 36 is

interposed in the conduit 34. The float valve includes a chamber 37 having an upper valve inlet opening 38 and containing a float 39 which supports a plug 40 for closing the inlet 38. The float 39 is freely supported within the walls of the chamber 37 and is guided for vertical movement on an up-standing tube 41 secured in the bottom of the chamber 37. The tube 41 also serves as a discharge opening from the chamber.

In operation, the reagent 12 spills through the inlet 38 into the valve chamber 37 at a rate much faster than the reagent can be passed through the metering tube 31. As a result, the chamber 37 gradually fills, causing the float 39 to rise until the plug 40 closes the valve inlet 38. Thereafter, the level of the reagent 12 within the valve 36 remains constant. As soon as a small amount of reagent passes through the metering tube 31 and out of the chamber 37, the plug 40 slightly opens the inlet 38 and that amount of reagent is immediately replaced. As a result, a constant head pressure on the reagent at the metering tube is established. The reagent head pressure and the length and diameter of the capillary metering tube 31 are such that a reagent flow rate into the passage 24 of 0.1 ml./min. is established. It will also be noted that the head established by the float valve 36 is greater than the sample head established by the overflow outlet 27 and thus the sample in the passage 24 is not forced upwardly through the capillary metering tube 31.

A disturbing problem which could affect the operation of the analyzer 10 is the presence of air bubbles within the passage 24 and metering tubes 21, 31. These air bubbles primarily result from air dissolved in the sample fluid which is released by the warming of the fluid as it passes into the room in which the analyzer is located or by the decrease in air solubility of the sample caused by the chemical reaction with the reagent 12. To minimize the effect of air bubbles, a strainer 45 is interposed in the passage 24 so that the fluid sample 11 must pass through the fine holes in the strainer before reaching the capillary metering tubes. This blocks the bubbles from the tubes 21, 31. Furthermore, the entire frame 25 is tilted so that air bubbles tend to remain trapped at the end of the passage 24 adjacent the strainer 45 and the connection point of the sample conduit 22.

As for turbidity particles in the sample 11 or reagent 12, it has been found that by disposing the capillary metering tubes 21 and 31 in generally vertical directions and by establishing the fluid flow through these tubes from top to bottom, the tendency of turbidity particles to clog the tubes is greatly minimized.

For the purpose of mixing and briefly

5 detaining the sample-reagent stream for
colourimetric testing, the stream is dripped
into a generally vertical transparent mixing
cell 50 disposed in the colourimeter 15. The
transparent cell 50 is formed with an open
bottom and open top and is mounted in
a surrounding transparent chamber 51 having
an overflow outlet 52 disposed well above
the open bottom of the cell 50. A nozzle 53
10 extends from the discharge end of the capillary
metering tube 21 to a position over
the open top of the cell 50 so that the
sample-reagent stream is dripped downwardly
into the cell 50 where it flows down through
15 the cell, out through the open bottom of the
cell, up through the surrounding chamber 51,
and out through the overflow outlet 52.
The mixture is then directed to a conduit
54 leading to the drain 30.

20 The dripping of the sample-reagent stream
into the cell 50 causes complete mixing of
the sample and the reagent, and the slow
flow of the mixture down through the cell
and up through the surrounding chamber 51
25 detains the mixture for colourimetric testing
while maintaining a constant and uniform flow
of the mixture under test. Alternatively,
mixing of the sample and reagent in the
cell 50 can be accomplished by using a motor
30 driven stirrer or some other mechanical
device, in which case the sample-reagent
stream need not be dripped into the cell.

To detect a colour-producing reaction in
the sample-reagent mixture, the colourimeter
35 15 includes a lamp 60, condensing lens 61,
shutter 62, colour filter 63 and photoelectric
cell 64, all arranged in the conventional
manner to direct a beam of light through
the fluid mixture downwardly through the
40 cell 50. The output of the photoelectric cell
64 is coupled through an adjustable resistance
65 to the galvanometer 16. The wiring circuit
also preferably includes a plug socket 66
coupled in parallel to the resistance 65 for
45 permitting a continuous recorder to be added
to the electrical circuit so that the output
of the photoelectric cell 64 can be used to
produce a continuous record.

Alternatively, the output of the colouri-
50 meter photoelectric cell 64 can be used to
trip a relay for controlling another piece of
apparatus. In this way the analyzer 10 can
perform as a monitor. Thus for example the
analyzer may be set up to automatically re-
55 generate a zeolite-type of water softener. In
such a use, the reagent 12 is EDTA
(ethylene diamine tetra acetic acid) plus a
pH buffer and an indicator such as Erio
Chrome Black T solution with the amount
60 of EDTA selected so as to reach the equi-
valence point and produce a colour reaction
at the desired hardness level at which the
water softener is to be regenerated. A red
filter 63 is used in the colourimeter 15
65 and the sample conduit 22 is connected to

the output of the water softener. As the
water softener becomes less and less effective
and the hardness of the water increases
beyond the selected cut-in point, the sample-
70 reagent mixture in the cell 50 turns from
blue to red so that the photoelectric cell
64 is activated to produce a current. This
current is then utilized to trip a relay and
either sound an alarm or automatically begin
75 the regeneration of the water softener.

By using appropriate reagents 12, the
analyzer 10 can also be used for detecting
pH or residual chlorine levels in water. It
will also be understood that more than one
80 reagent can be added to the sample under
test simply by using two or more reagent
supplies with associated float valves and
capillary metering tube assemblies. Such a
two-reagent unit has been found suitable for
85 testing fluoride levels in water using a Megre-
gian Maier form of test reaction.

It is of significance to note that the
reagent metering tube 31 opens into the
passage 24 ahead or upstream of the meter-
90 ing tube 21. This enables the reagent 12
to include small amounts of an anti-mould
and slime agent such as formaldehyde as
well as a formulation for preventing mineral
deposits so as to resist fouling of both of
95 the tubes 21 and 31. However, if tube foul-
ing is not a problem, the analyzer 10 can
function properly with the reagent metering
tube 31 opening into the sample stream below
or downstream of the tube 21.

In accordance with a further aspect of
100 the invention, the method of testing described
above can be modified for continuously per-
forming spectrophotometric titration by using
a titrant as the reagent added to the sample
stream, adding also a constant and uniform
105 flow of an indicator, and alternately reducing
and increasing the amount of titrant added
to the sample stream so as to bring repeatedly
the mixture in the colourimeter cell to end
point. That is, the flow of titrant is con-
110 tinuously adjusted so that each time the indi-
cator produces a colour change showing that
end point of the titration has been reached,
the flow of titrant is reduced below the
colour change producing end point. When
115 the colour change again reverses, the titrant
flow is increased again to bring about an
end point reaction.

By continuously increasing and reducing
120 the proportion of titrant added to the steadily
flowing sample so as to cause oscillating
colour changes in the sample-titrant-indicator
mixture, a continuous titration is run on
the flowing sample. By knowing the sample
125 flow rate and the strength and character of
the titrant, and by noting the titrant flow
rates required to produce the oscillating colour
changes, the results of the titration can be
easily calculated.

To carry out this further aspect of the 130

invention, an analyzer 10a shown in Figure 2 is provided including apparatus for accomplishing continuously the several steps referred to above as capably to perform the method according to the invention. In describing the analyzer 10a, those parts similar to those described in connection with the analyzer 10 in Fig. 1 have been given identical reference numerals with the identifying suffix "a" added.

The analyzer 10a acts upon a sample 11a which is transmitted to a capillary metering tube 21a through a conduit 22a having a flow-control cock 23a. The sample 11a passes from the cock 23a into a mixing passage 24a and through a strainer 45a. A frame 25a supports the metering tube 21a and the associated structure.

An overflow outlet 27a establishes the sample pressure head in the passage 24a and a conduit 29a is provided for carrying the overflowing sample to a drain opening 30a. A sight glass 28a indicates the sample head.

For adding titrant 12a to the passage 24a, the titrant is supported in a bag 32a and is conducted through a conduit 34a to a capillary metering tube 31a which opens into the passage 24a. A sight glass 35a visually indicates the supply of titrant 12a remaining in the bag 32a.

To maintain a predetermined head pressure on the titrant 12a at the metering tube 31a, a float valve 36a is interposed in the conduit 34a. The float valve 36a functions internally as does the float valve 36 described above. Also interposed in the conduit 34a is a filter 70 to prevent solid particles from being lodged in the capillary metering tube 31a.

In addition to the sample 11a and titrant 12a, an indicator 71 is also added to the stream under test. For adding the indicator 71 to the sample-titrant stream, a supply of indicator is disposed in a plastic bag 72 carried within a carton 73, and a conduit 74 couples the bag 72 to a capillary metering tube 75. Preferably, a filter 76 is interposed in the conduit 74. A sight glass 77 is provided to visually indicate the amount of indicator 71 remaining in the bag 72.

The head pressure on the indicator 71 and the length and diameter of the metering tube 75 are selected so that an indicator flow rate through the metering tube of about 0.1 ml./min. is achieved. This flow rate is not particularly critical and will vary as the indicator 71 empties from the bag 72. A valve similar to the valve 36a can, if desired, be interposed in the conduit 74 to stabilize the indicator flow rate. A conduit 78 connects the lower output end of the metering tube 75 to a nozzle 53a which feeds the sample-titrant-indicator stream to a colourimeter 15a.

For mixing and briefly detaining the fluid

stream from the nozzle 53a in the colourimeter 15a, a vertical transparent cell 50a having an open top and open bottom, surrounded by a transparent chamber 51a having an overflow outlet 52a, is provided. The overflow outlet empties into a conduit 54a which leads to the drain 30a. The colourimeter 15a includes a lamp 60a, condensing lens 61a, shutter 62a, filter 63a and photoelectric cell 64a all arranged in the conventional manner to transmit a beam of light through the fluid mixture passing downwardly through the cell 50a. The operation of the cell-surrounding chamber 51a and overflow outlet 52a in establishing a uniform continuous flow of the mixture under test through the colourimeter 15a is as described above in connection with the apparatus of Figure 1.

In order to change the flow rate of the titrant 12a and thus cause oscillating colour changes in the cell 50a, the float valve 36a is vertically adjustable and the output of the colourimeter photoelectric cell 64a is used to vary the vertical position of the valve 36a and thus vary the head pressure on the titrant at the metering tube 31a. In this way, the flow rate of the titrant added to the stream of sample 11a in the passage 24a is varied. In the illustrated construction, the valve 36a is mounted on a bracket 80 which is threaded on a lead screw 81 journaled at 82 and 83 in the analyzer 10a. The screw 81 is rotatably driven by a motor 84 through a worm 85 and gear 86.

The motor 84 is continuously driven and the photoelectric cell 64a, through an amplifier 87, drives a relay 88 which controls the direction of rotation of the motor 84 (see Figure 3). In the embodiment shown in Figure 2, the amplifier 87 and relay 88, together with appropriate fuses and on/off switches, are enclosed within a box 89.

To permit the float valve 36a to be raised and lowered by running the bracket 80 up and down the lead screw 81, the conduit 34a is flexible and of a sufficient length to provide the desired range of movement of the float valve.

To illustrate the function of the analyzer 10a, it will be assumed that the analyzer has been set up to measure the total hardness of a water stream within a range of zero to 250 parts per million. The titrant 12a is preferably a standard EDTA solution in a concentration suitable for the selected range of hardness. A standard hardness buffer-indicator is used as the indicator 71 which normally produces a red colour when added to the water-EDTA solution but which turns blue at the titration end point indicating a complete reaction between the water hardness elements and the EDTA solution. A red filter 63a is employed.

When the operation of the analyzer 10a

adjusted as described above is begun, the colour in the colourimeter cell 50a is red so that the photoelectric cell 64a receives radiation and produces an electrical output which is amplified by the amplifier 87 and is effective to operate the relay 88. With the relay 88 picked up, the continuously energized motor 84 is driven in a direction so as to cause the lead screw 81 to raise the bracket 80 and thus lift the float valve 36a. As the float valve 36a rises, the rate of titrant flow into the passage 24a is increased until the increased amount of titrant causes the titration end point to be reached and the fluid mixture in the cell 50a to turn blue. The filter 63a absorbs the blue light passing through the fluid in the cell 50a so that the photoelectric cell 64a ceases to be activated whereupon the relay 88 drops out and the motor 84 is reversed to drive the bracket 80 and thus the float valve 36a downwardly.

Downward movement of the float valve 36a causes a decrease in the flow rate of the titrant into the passage 24a until the mixture in the cell 50a goes past the end point of the titration reaction and the solution again turns red with the result that the photoelectric cell 64a is again activated and the motor 84 reversed.

The apparatus 10a thus embodies a form of oscillating feedback, with the raising and lowering of the valve 36a causing colour oscillations in the fluid mixture being sensed in the colourimeter cell 50a. The colour oscillations in turn produce the raising and lowering motion of the float valve 36a. In the illustrated embodiment under discussion, it requires about five minutes to produce a reversal of the motor 84 and the range of travel of the float valve 36a is approximately one quarter of an inch.

To enable the results of the titration performed by the analyzer 10a to be read directly, a scale 91 and pointer 92 are associated with the vertically movable bracket 80 so as to indicate the position of the float valve 36a and thus the relative head pressure of the titrant 12a. The scale 91 is calibrated so that the position of the valve 36a is translated directly into terms of the amount of unknown in the sample being tested. In the example being discussed herein, the scale 91 thus reads in total hardness values from zero to 250 p.p.m.

So as to obtain an average reading as the valve 36a oscillates up and down, a lost-motion connection is provided between the pointer 92 and the bracket 80. In the illustrated embodiment, the bracket 80 carries a pin 93 which moves between spaced bumpers 94 and 95 carried by the pointer 92. The pointer is frictionally supported on the scale 91. The spacing between the bumpers 94, 95 is approximately the normal

oscillating distance of the float valve 36a, that is, one quarter of an inch in the present example. The pointer 92 thus stands stationary so long as the sample 11a remains constant and the float valve 36a simply oscillates back and forth. As soon as the amount of unknown changes in the sample 11a, the movement of the float valve 36a is also correspondingly changed and the position of the pointer 92 is modified to correspond to the change detected in the sample 11a.

Alternatively, the scale 91 and pointer 92 combination can be replaced by a slide wire resistor with the sliding contact being carried by the bracket 80 and the resistance wire extending alongside of the lead screw 81. In this way, the vertical position of the float valve 36a can be made to control a variable electrical output and this output can be coupled to an electrically-responsive recorder of standard type to produce a continuous record of the titration operation performed by the analyzer 10a.

The analyzer 10a can also be employed, in addition to testing for total hardness in water, for performing silica and alkalinity analysis on water. It is also obvious that other titration procedures can be automatically and capably performed by the analyzer 10a simply by utilizing proper titrants and indicators.

The analyzers 10 and 10a are relatively simple in design and hence adapted for economical manufacture and operation. The fact that few moving parts such as pumps or valves are utilized in the construction of the analyzers means that few operating difficulties are encountered so that the units are quite reliable and require little routine maintenance.

WHAT I CLAIM IS:—

1. An automatic analyzer which comprises means for feeding a stream of a sample at a constant head through a first capillary metering passage, means for feeding a stream of a reagent at a determined head through a second capillary metering passage into the sample stream at a position upstream or downstream of the first passage and separated from the first passage by a passage of non-metering dimensions, means for mixing the sample-reagent stream, and means for detecting a reaction in the mixed sample reagent stream.

2. An automatic analyzer according to claim 1, in which the means for detecting a reaction comprise a colourimeter having means for maintaining a constant and uniform flow of the sample-reagent mixture through the colourimeter cell.

3. An automatic analyzer according to claim 2, in which the colourimeter comprises a transparent generally vertically disposed cell having an open top and bottom, a trans-

parent chamber surrounding the cell, the lower end of the cell opening into the chamber, an overflow outlet formed in the chamber above the lower end of the cell, and means for dripping the sample reagent stream into the cell so as to mix the sample and reagent.

4. An automatic analyser according to any one of the preceding claims comprising means upstream of the means for mixing the sample reagent stream, for feeding in a stream of an indicator, means for detecting a reaction in the mixed stream indicative of an end point, and means, responsive to the detecting means, for varying the head of the reagent so that the head is continuously alternately raised and lowered to bring the mixed stream repeatedly to the end point.

5. An automatic analyzer according to claim 4 including a scale for indicating the head of the reagent and thus the amount of reagent required to bring about the end point reaction.

6. An automatic analyser according to claim 5, in which the means responsive to the detecting means are connected to an indicator on the scale through a lost motion device so that the average head of the reagent is indicated.

7. An automatic analyzer according to any one of the preceding claims for continuously performing a colourimetric test on a sample comprising, a frame defining a fluid passage, a first conduit for conducting a flow of the sample to the passage at a constant head pressure, a first capillary metering tube mounted in the frame and opening at one end into the passage, a second conduit for conducting a constant flow of the reagent to the other end of the first metering tube at a head pressure greater than the sample head, a second capillary metering tube mounted in the frame and opening into the passage, a colourimeter including a transparent cell, a third conduit coupling the second metering tube with the cell so that the sample and reagent is uniformly dripped into the cell and mixed, means for maintaining a constant and uniform flow of sample-reagent mixture through the cell, and means for indicating the output of the colourimeter.

8. An automatic analyzer according to claim 7 including a float valve interposed in the second conduit for maintaining a head pressure on the reagent in the metering tube,

the float valve being higher than an overflow outlet in the first conduit so that the reagent head is greater than the sample head.

9. An automatic analyzer according to claim 7 or claim 8 including a strainer mounted so that the sample flows through the strainer.

10. An automatic analyzer according to any one of claims 7 to 9 in which the fluid passage in the frame extends generally from one end of the frame to the other and including means interposed in the second conduit for establishing a variable head pressure on the reagent in the metering tube the second capillary tube opening at one end into the end of the passage that is opposite the first conduit connection.

11. A method of continuously performing a test on a sample comprising the steps of creating a steady and uniform stream of the sample, adding to the stream a determined flow of a reagent, dripping the sample reagent stream into a cell so as to mix the stream, flowing the sample reagent mixture constantly and uniformly through the cell, and detecting any reaction caused.

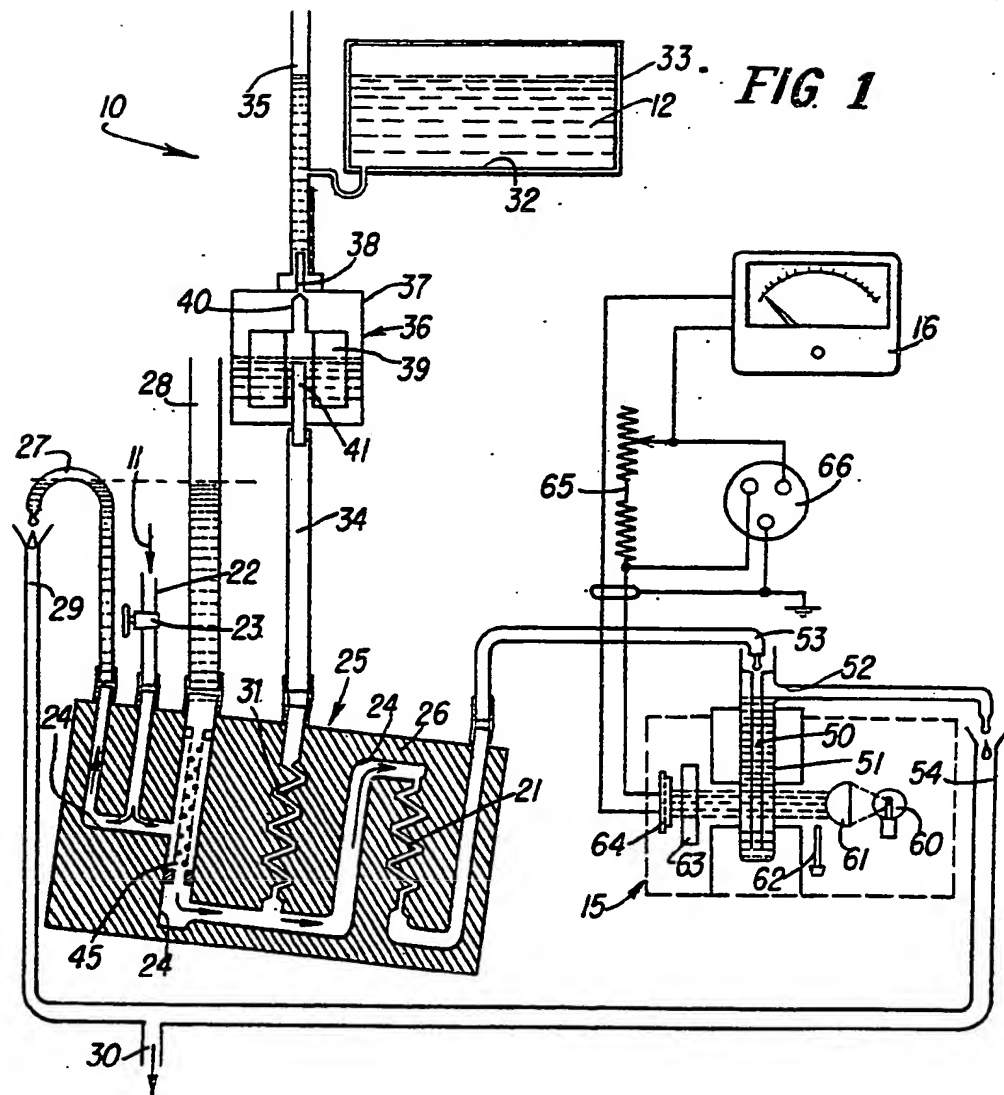
12. A method according to claim 11 of continuously performing a colourimetric test on a sample in which the cell is transparent and a beam of light is passed through the cell to detect the light transmitting qualities of the sample reagent mixture.

13. A method of performing continuous titration on a sample comprising the steps of creating a steady and uniform stream of the sample, adding to the stream a determined flow of a reagent, adding to the sample reagent stream a flow of an indicator, mixing the sample reagent indicator stream in a cell, flowing the mixed stream constantly and uniformly through the cell, detecting an end point reaction in the cell, and alternately reducing and increasing the amount of reagent added to the stream so as to repeatedly bring the mixture in the cell to end point.

14. An automatic analyzer substantially as hereinbefore described and illustrated in Figure 1 or Figures 2 and 3 of the accompanying drawings.

15. A method of testing a sample substantially as hereinbefore described with reference to Figure 1 or Figures 2 and 3 of the accompanying drawings.

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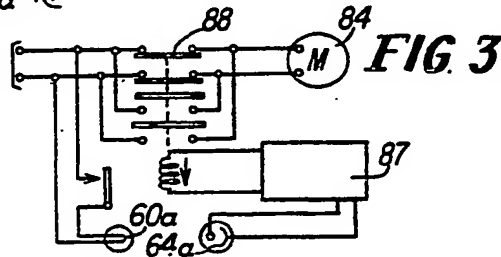
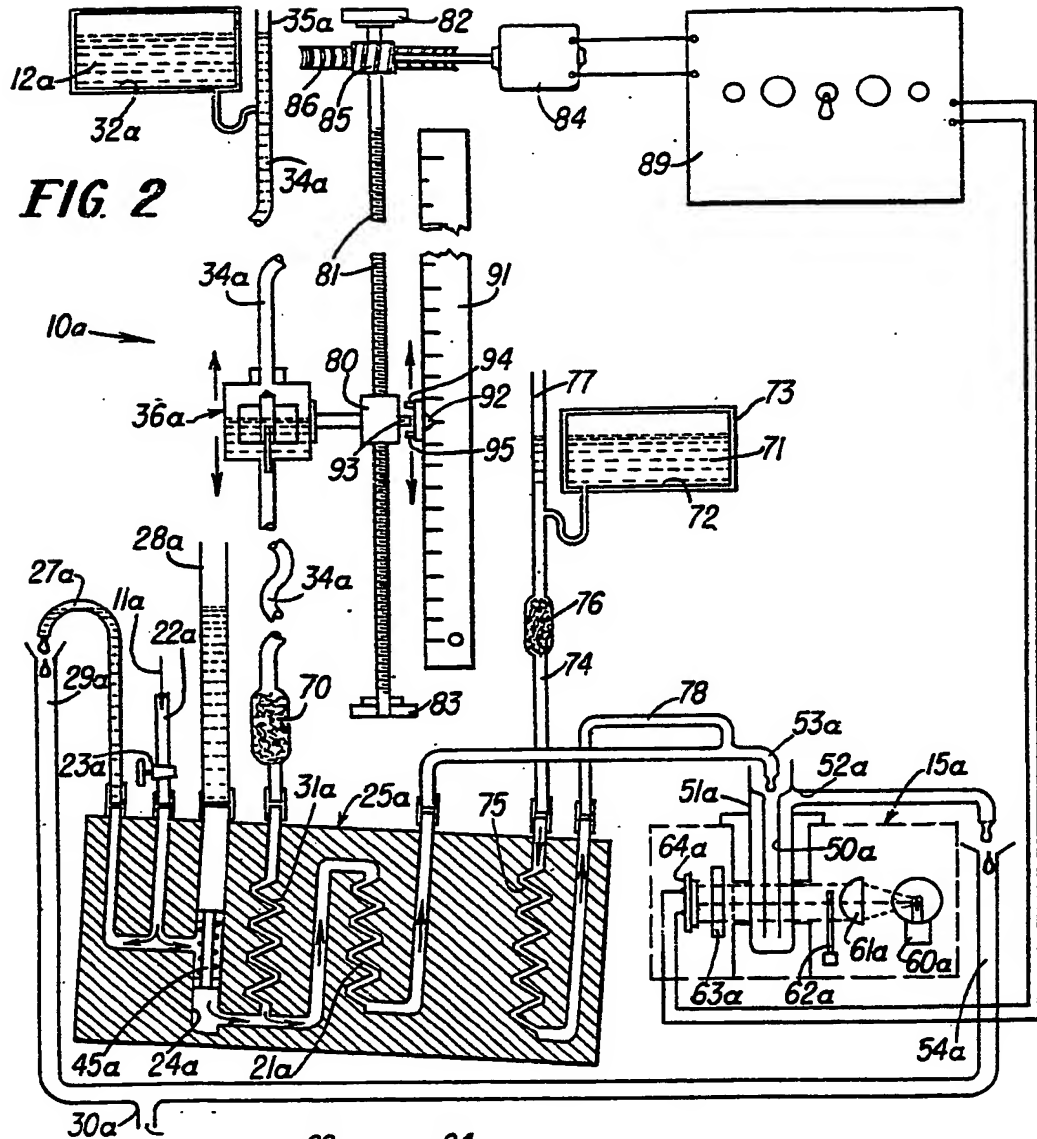


FIG 1

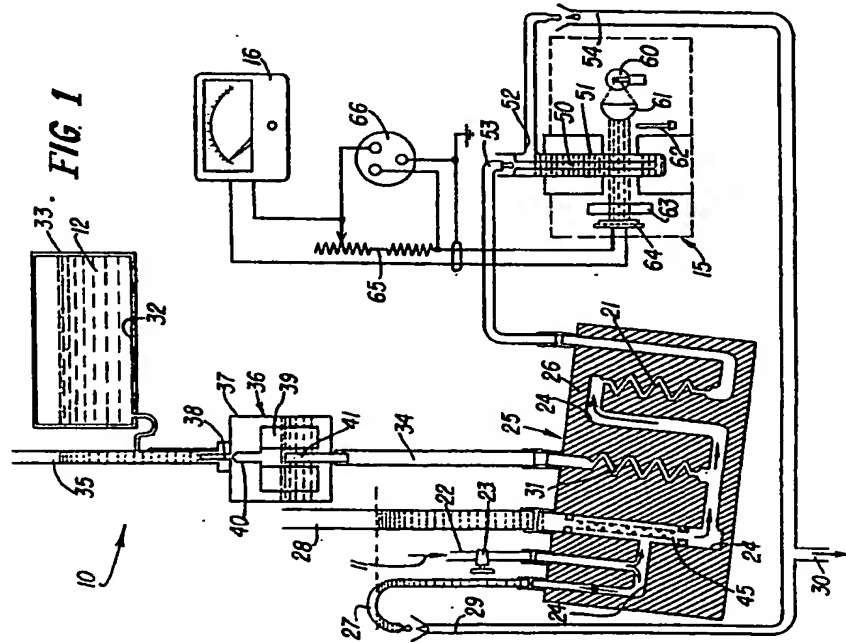


FIG 2

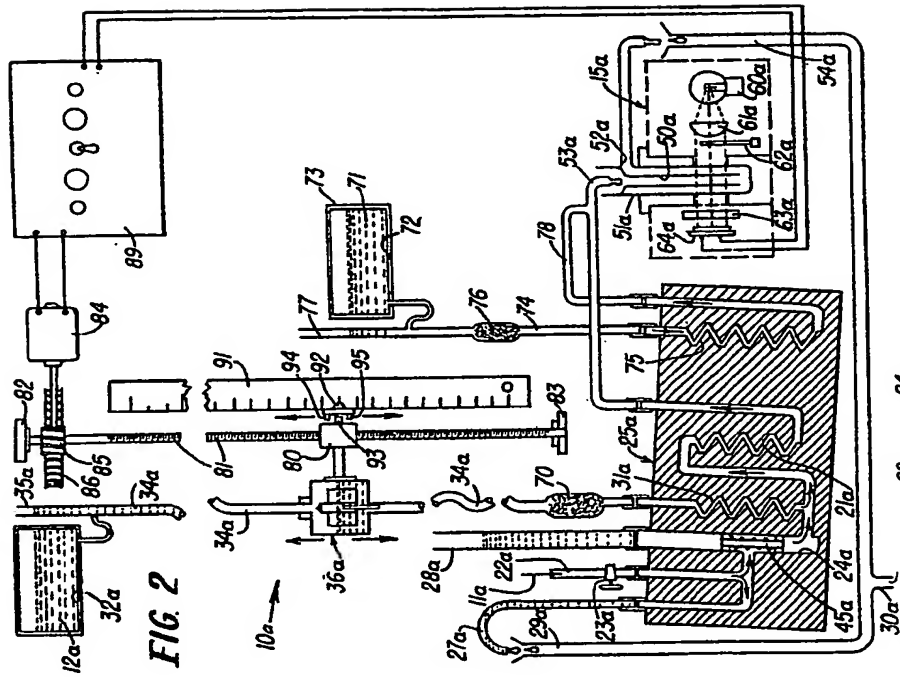
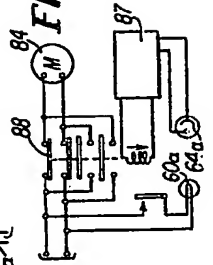


FIG 3



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